A New Method for Studying Ionising Potentials.

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Introduction.

It is evident that an exact knowledge of the energy necessary to remove the electrons from a molecule is of great value in formulating definite ideas of atomic structure and in testing the correctness of any quantitative theory. Not only is it desirable to know the work required to detach the outermost valence electron but also the further energy steps corresponding to the removal of more closely bound electrons. Moreover, in the case of polyatomic molecules, it would be most interesting to learn what the actual products of ionisation are, whether it is necessarily accompanied by dissociation and, if so, what is the state of the dissociated components.

In ionisation of a gas by the impact of slowly moving electrons we have a method of disrupting molecules under known energy conditions, and therefore turn to experiments of this type for the solution of the problems just propounded. The first important quantitative work was that of Franck and Hertz* in 1913 using a method originally due to Lenard. Modifications and improvements in this general mode of attack have enabled subsequent investigators to contribute greatly to knowledge of atomic structure. For a detailed discussion of methods and results reference can be made to Hughes' "Report on Photo-electricity"† or to a recent series of papers by Franck,‡ but for the purpose of the present paper it will be sufficient to state the principal results as briefly as possible.

It has been proved that there are various critical energies which an impacting electron can transfer to an atom, and that such a transference causes the atom either to eject one or more electrons entirely, becoming an ion or merely to change to a condition of higher potential energy, giving off radiation on its return to the normal state. In the cases of the monatomic gases and the metallic vapours the critical energies directly observed can often be interpreted in terms of electron transitions by comparison with spectroscopic experiments and the application of Bohr's theory of stationary states. Thus, the lowest ionising potential undoubtedly gives the energy necessary to remove one electron from the atom and agrees with the value from the known spectral series relations. For the higher degrees of ionisation, however, such indirect methods of interpretation become more difficult, and it is only in a few special cases that any success has been achieved. Similarly, in the case of the polyatomic molecules the complicating factor of dissociation is so troublesome and spectroscopic evidence so meagre that the theoretical interpretation of experimental results is usually doubtful.

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* J. Franck and G. Hertz, 'Verh. d. D. Phys. Ges.,' vol. 15, p. 34 (1913).

† A. L. Hughes, 'Bull. National Research Council,' April, 1921.

‡ J. Franck, 'Phys. Zs.,' vol. 22, pp. 388–391, 409–414, 441–448, and 466–471 (1921).

The difficulty with the ordinary methods is that they are merely able to detect ionisation without giving any direct evidence as to what is being ionised or what the products are. Though it is sometimes possible by indirect means to distinguish between single and double ionisation or between molecular and atomic effects, it would be very advantageous to get a direct method of analysing the products of the ionisation tube.

Positive ray analysis as originated by Sir J. J. Thomson and developed by Aston and Dempster provides a method for determining the ratio of mass to charge, while the ordinary ionising potential experiments furnish a method for producing ions under known energy conditions. The combination of these two methods of analysis, therefore, should provide much more complete information. Unfortunately, such a combination presents serious difficulties. For the results of the positive ray analysis to be of any value, the mean free path of the ion must be comparable with the distance between the place of formation and its place of detection, since any collisions on the way might change the nature of the ion and thus invalidate the measurements of its formation energy. On the other hand, at the place of formation of ions the molecular and electronic densities must be sufficient to produce a detectable number of ionising collisions. Thus, the difficulty is to obtain the maximum number of molecules and electrons in one small region and as few as possible elsewhere. The ordinary arrangement of a hot filament and electrical fields confines the electrons within proper bounds and a unidirectional molecular stream such as is used in a mercury diffusion pump offers a possibility of localised high vapour density.

The experiments which will now be described are the first steps along the line of attack indicated in the preceding paragraphs. Mercury was selected as the most suitable substance for the initial experiments because it lends itself easily to the production of a unidirectional molecular stream and because its ionising potential is so well known. Its high molecular weight was also found of advantage in distinguishing its effect from that of light gaseous impurities.

Apparatus.

In discussing the apparatus, the main part of which is shown in fig. 1, the method of introducing mercury vapour will be described first. A continuation (not shown) of the tube above A, at the top of the drawing, was bent through 180° and led to the mercury reservoir which was heated electrically. A small tube B also led to the reservoir, but had a trap in it to prevent vapour from passing. Thus, mercury vapour coming from the reservoir entered at A into the region cooled by the circulation of water in the coil C. Much of it condensed on the walls, was caught in the trap T, and returned to the reservoir through B. A small portion, however, consisting of molecules whose thermal velocities were approximately parallel to the walls of the tube, passed down through T. Before getting to the second trap, U, many of these molecules diffused to the walls, but since the latter were cooled by freezing mixture in the cooling jacket, J, the probability of molecules rebounding from them was small. Consequently, the only molecules which were likely to pass through the trap U into the ionisation tube proper were those which passed

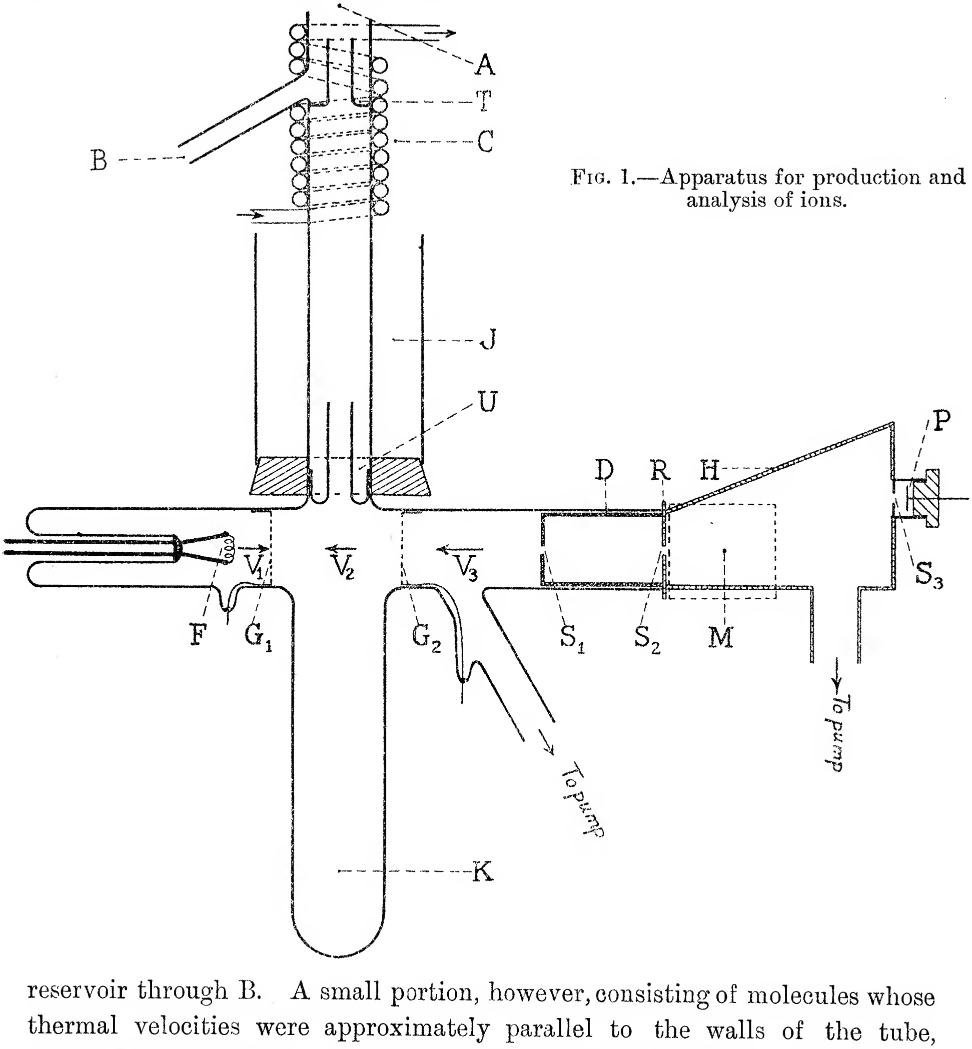

FIG. 1.—Apparatus for production and analysis of ions.

straight downward between the gauze electrodes, G_1 and G_2, into the condenser, K, which was immersed in liquid air. In this way general diffusion of mercury vapour throughout the apparatus was reduced to a minimum. Originally only the trap U was used, but it was impossible to arrange an outlet for it and it filled up rapidly. The introduction of a second trap with a return tube to the reservoir made it possible to use the apparatus continuously.

Through the side tubes shown, the apparatus was connected by $\frac{3}{4}$-inch tubing to a two-stage mercury condensation pump. The fore vacuum was produced by an oil pump in the early part of the work, but was later improved by the introduction of a Gaede rotary mercury pump. The pressure was measured on a McLeod gauge reading down to about 10^{-5} mm. Hg, and when the pumps were going there was no difficulty in keeping below this pressure, but there remained always a slight leak, presumably in the positive ray chamber, so that on standing overnight the pressure would go up to about 0·001 mm. A liquid air trap prevented mercury vapour from getting back to the apparatus from the gauge and pumps. Though the presence of wax joints made it impossible to bake out the whole apparatus, the mercury was first introduced in a supplementary reservoir so that the final reservoir could be baked out and then the mercury slowly distilled over into it under high vacuum.

The arrangements so far described furnished a fairly high and well localised density of mercury molecules between the platinum gauzes G_1 and G_2. We will now consider how some of these molecules were ionised, and the nature of the ions determined.

Electrons from the tungsten filament, F, were accelerated by the small field V_1 and then retarded by the equal field V_2, so that they would collide with the molecules between the gauzes at velocities between V_1 and zero (neglecting velocity of emission). The field V_2, besides preventing electrons from going beyond G_2, served to extract any positive ions formed. These were then further accelerated by the much larger field V_3 till they came to the slit S_1. The two slits, S_1 and S_2, of width 2 mm., served to define a beam of ions which then passed between the pole-pieces, M, of a small electromagnet, and were consequently deflected so that those of a particular value of m/e fell on the slit S_3 of width 3 mm. Behind this slit was the insulated plate, P, which was connected to a Compton electrometer kindly loaned to the author by the Department of Physics, at Princeton. The sensitivity of this instrument, as used, was about 4,000 divisions per volt.

The main part of the positive ray chamber, H, was of heavy brass, and was joined to the glass part of the apparatus at the flange, R, with sealing-wax. The cylinder, D, which extended into the glass tube, was of iron, so that the ions between S_1 and S_2 were shielded from the stray magnetic field. As the drawing of fig. 1 is not strictly to scale the most important dimensions are given below:—

Diameter of ionisation tube	2·2 cm.	
„ aperture in traps T and U	0·7 „	
„ tube containing traps	1·7 „	
Length of „ „ „	20 „	(Reduced in drawing.)
Diameter of condenser K	2·7 „	
Length of „	15 „	
Distance from F to G_1	0·4 „	(Exaggerated in drawing.)
„ „ G_1 to G_2	3·5 „	
„ „ G_2 to S_1	5·8 „	(Reduced in drawing.)
„ „ S_1 to S_2	4·6 „	
„ „ S_2 to S_3	8·5 „	
Area of poles of magnet	3·3 × 2·5 cm.	
Distance apart of poles of magnet	2·1 cm.	

The procedure adopted was to set the voltages, filament current, heating current, etc., and then measure the rate of charging of the electrometer as the current through the electromagnet was varied. Readings were always taken with increasing magnet current, and before each run the current was reversed several times. The magnetic field, corresponding to a given current, was read from a calibration curve obtained with a fluxmeter and coil. The electrometer readings were plotted against the magnetic fields so obtained.

After the apparatus was taken down the magnetic field was redetermined with a triangular coil, as described by Sir J. J. Thomson.* Within the limits of error these measurements gave the correct value of m/e for doubly-charged mercury ions, but a somewhat low value for the singly charged. This was presumably due to the fact that the coil used was not long enough to measure entirely the effect of the stray field, which was more marked at the higher values of the magnetic field required to bend the singly-charged ions. Incidentally, the stray field did valuable service by preventing any photo-electrons liberated at the end of the cylinder, D, around S_1, from getting back toward G_2 and causing spurious ionisation effects.

Results.

The wide slits used to get maximum intensity, together with the comparatively small magnetic field, made it impossible to get great resolution, but it was hoped that it would at least be possible to distinguish between singly- and doubly-charged mercury ions. It was found, however, that the effect of the single ions was so great, compared to that of the double at low voltages, that often the curves were of the type of A, fig. 2, showing both types of ion, but not completely separated. In curve B, on the other hand, where the value of V_1 was 80 instead of 40 and the cooling was better, the two effects are separated. In this curve there also appear two, and possibly three, other maxima of values of m/e approximately 15, 35, and 50, on the scale of $m/e = 1$ for hydrogen. These will be discussed in connection with a later curve.

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* J. J. Thomson, 'Rays of Positive Electricity,' p. 18, 2nd edition (1921).

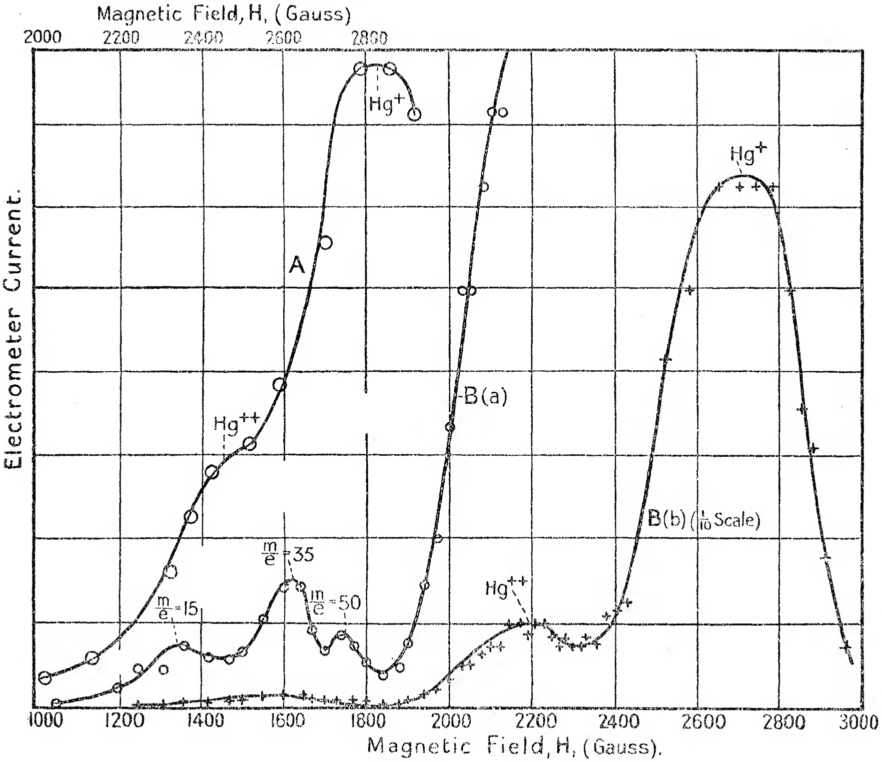

Fig. 2.

Curve A. $V_1 = -V_2 = 40$ volts. $V_3 = 620$ volts.
" B. (*a*) $V_1 = -V_2 = 80$ volts. $V_3 = 520$ volts.
(*b*) Same run on 1/10 scale.

In fig. 3 a group of curves taken at higher values of V_1 is presented. In order to make readings possible these runs had to be made with very much reduced filament currents. The striking feature of these curves is the complete separation between the Hg^+ and Hg^{++} peaks, and the greatly increased relative intensity of the latter. In curves C and D again appear two peaks at low values of the magnetic field, H, and in D, where the maxima are unusually sharp, there is a small but definite maximum at $m/e = 65$ approximately. The effects at $m/e = 15$ and 30 are evidently due to the presence of a trace of air, and possibly other gaseous impurities. There was known to be a very small leak, and it was noticed that these peaks were always particularly strong when the pumps had just been turned on in the morning. Moreover, the addition of the Gaede pump in the fore vacuum greatly reduced their intensity, and it was found that on reducing V_1 they disappeared between 15 and 20 volts. The peak at $m/e = 65$ is naturally attributed to triply-charged mercury, and it is possible that mercury ions of higher charges are present but masked by the air peaks, just as it is difficult to identify with certainty

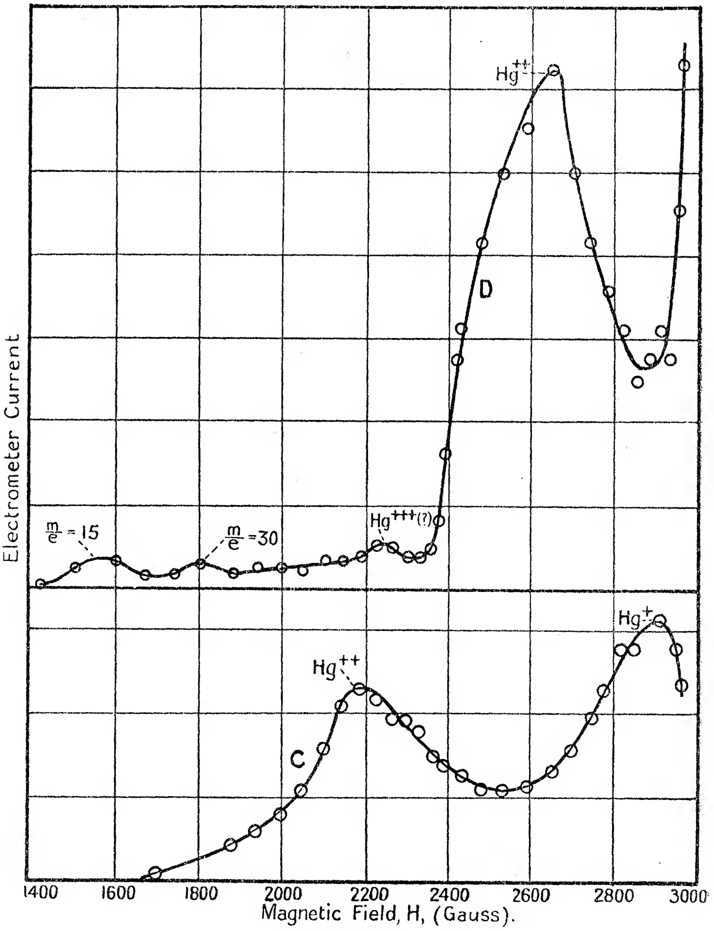

FIG. 3.

Curve C. $V_1 = -V_2 = 300$ volts. $V_3 = 300$ volts.
„ D. $V_1 = -V_2 = 175$ „ $V_3 = 610$ „

an $m/e = 65$ peak in the other curves. In any case, the number of more highly-charged ions is extremely small compared to that of the single and double, even when the voltage is run up to 500, and may be due to impacts among the ions themselves rather than to electron bombardment. It is, therefore, impossible to draw any conclusions as to the conditions for their formation from the present experiments, though it is hoped that a more powerful apparatus may be able to throw light on the question. Similarly, the search for a polyatomic mercury molecule must wait for a larger magnet.

The curves shown and discussed, so far, are typical of some sixty or seventy runs made with values of V_1 varying from 10 to 500, and V_3 from 120 to 1290. These served to give valuable evidence as to the production of singly- and doubly-charged ions, and to indicate roughly the beginning of double ionisation at between 20 and 25 volts. It remained to locate this point as definitely as possible.

It is clear that by the time the electrons get to the point of maximum mercury density between G_1 and G_2 they will have been slowed down by the field V_2, so that their speed will be considerably less than V_1, but cannot be properly estimated. The procedure adopted, therefore, was to make a run in the usual way, then set the magnet current at the value for the Hg^+ peak, and reduce the value of V_1 till the effect had completely disappeared. Since the ionisation potential of mercury is known to be 10·4, the difference between this and the observed voltage, where all effect disappeared, was taken as a correction to determine the effective voltage for the original run. Of course, this automatically includes corrections for initial velocity, potential drop across the filament, space charge, etc. When this procedure was first adopted curves were obtained of the type of K, fig. 4, giving corrections of 4 or 5 volts, which was the expected order of magnitude.

In the course of a week's running the magnitude of this correction gradually increased until it was as large as 15 volts in two or three of the last experiments. This may be connected with the gradual filling up of the trap U, and the consequent improvement in the cooling of the inner walls of the trap. In this way the number of stray molecules was reduced, so that the impacting electrons had to pass through a greater proportion of the field V_2 before colliding with mercury molecules. Notwithstanding this variation, the corrected results were very consistent.

In fig. 4 are presented the results of four runs taken at accelerating voltages of 13, 16, 20 and 25 (corrected), with corrections of from 3 to 5 volts. In curves E and F there is no trace of the Hg^{++} peak, while in G it is small but distinct, and in J unmistakable, though the Hg^+ peak is now spreading out. Of twenty-four curves taken at effective voltages below 25, the eleven taken at 20 or above, with a single exception, definitely show the Hg^{++} peak. The exception was taken at 20, and also shows a trace of Hg^{++} but not very definitely. A group of five runs at about 17 volts are conflicting, as two show Hg^{++}, two do not, and one is doubtful, but these were taken without liquid air on the condenser or ice in the cooling jacket, and therefore are not of great value. On the other hand, with proper cooling two runs at 16 volts, two at 15, and one at 13, show no Hg^{++}, while in one

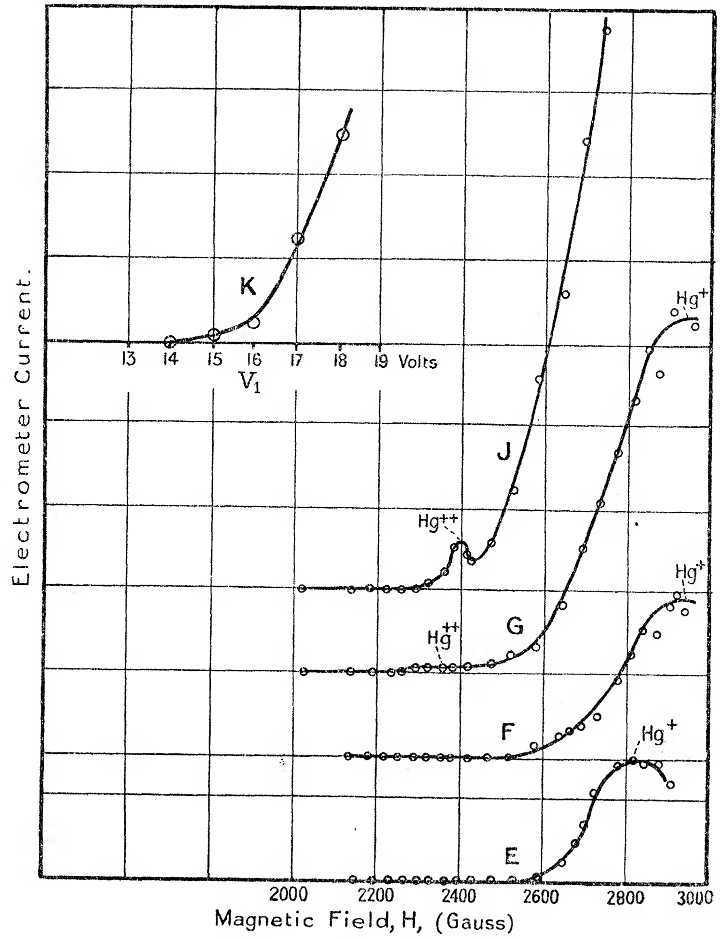

FIG. 4.

Curve E. $V_1 = -V_2 = 13$ (17) volts. $V_3 = 450$ volts.
„ F. $V_1 = -V_2 = 16$ (20) „ $V_3 = 490$ „
„ G. $V_1 = -V_2 = 20$ (25) „ $V_3 = 490$ „
„ J. $V_1 = -V_2 = 25$ (30) „ $V_3 = 480$ „
„ K. $H = 2820$ $V_3 = 460$. Correction curve for E.

Values of V_1 given are corrected. Uncorrected values in parentheses.

at 19·5 it is weak but definite, another at 19·5 does not show it, and a third curve at nineteen reveals just a trace of it. Three attempts to follow an Hg^{++} maximum to its vanishing point, with decreasing voltage, gave the results 22, 20 and 17 volts respectively. A consideration of these assembled results leads to the conclusion that doubly charged mercury ions are first produced when the electrons in the bombarding stream have attained an energy of 19 ± 2 volts.

Discussion of Results.

To appreciate the theoretical significance of the above results, it is necessary to review briefly some spectroscopic data. The enhanced spectrum of an element is supposed to be due to electron transitions in a singly ionised atom. Consequently, just as the principal series limit of the arc spectrum gives a basis for the calculation of the energy required to remove an electron from a neutral atom, so the corresponding series limit in the enhanced spectrum should give the energy necessary to remove an electron from a singly charged atom. This limit is not known for mercury, but has been determined approximately for zinc and cadmium, which are very similar to mercury spectroscopically. The limit of the principal doublet series of the enhanced spectrum of zinc is $\nu = 1\sigma = 147{,}544$, and of cadmium is $\nu = 1\sigma = 140{,}226$, where ν is the wave number.* Applying the quantum relation, $eV = h\nu c$, we obtain 18·2 volts and 17·3 volts for zinc and cadmium respectively. Now the single ion formation energies are 9·0, 9·4 and 10·4 volts for cadmium, zinc and mercury, and, by analogy, we should expect the double ion formation energy to be highest for mercury. Therefore the inference is that the energy required to remove a second electron from a singly charged mercury atom is of the order of 20 volts, and the energy necessary to eject two electrons at once from a neutral atom is $20 + 10·4$, or approximately 30 volts.

If, now, we consider the experimental value of 19 ± 2 volts given above, we are forced to the conclusion that the double ions were formed first as the result of two impacts, but that there remains the possibility that higher speed electrons produced double ions at one impact. In the experimental curves the separation of the two maxima was not good enough to allow the detection of a sharp increase in the number of double ions in the neighbourhood of 30 volts. On the other hand, the curves at high voltages and low electron currents, *e.g.*, C, fig. 3, show almost as many double ions as single, indicating that, under such conditions, the majority of the double ions were produced by single impacts. This conclusion is supported by the fact that the ratio of the double ion effect to the single ion effect showed no consistent variation with the electron current.

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* A. Fowler, 'Series in Line Spectra,' pp. 142, 146 (1922).

It is interesting to note that, in an attempt to detect double ionisation of mercury by a sharp increase in the total ionisation current, Einsporn* got kinks in his curves at about 17 volts and 42 volts. He attributes that at 17 to the presence of gaseous impurities, and is doubtful about the interpretation of the one at 42. In the light of the present experiments, it seems possible that the effect in the neighbourhood of 17 volts may have really been due to doubly charged mercury ions. The meaning of the 42-volt break remains doubtful.

It seems best to postpone any further discussion or speculation suggested by these results until further data are available. At present an attempt is being made to apply the method to gases, and a systematic investigation of the metallic vapours is reserved for the future.

Summary.

1. A new mode of attack on ionising potential problems is suggested. The principle involved is the study, by positive ray analysis, of the ions produced in a gas by the impact of slow-speed electrons of known energy.

2. The details of the application of the method to the study of mercury vapour are given.

3. Preliminary results indicate the formation of doubly charged mercury ions at 19 ± 2 volts. The series relations of the enhanced spectrum of mercury are not known, but analogy with zinc and cadmium suggests an estimate in agreement with the above value. The conclusion is that the double ions formed at this voltage are the result of two impacts. Experiments at higher voltages indicate formation by single impact.

4. More highly charged ions were present in such small quantities that their identification was uncertain, even at voltages as high as 500.

In conclusion, the author wishes to express his sincere thanks to Sir Ernest Rutherford for his continued and helpful interest and for the privileges of the laboratory, and also to Dr. Aston for some valuable suggestions. The work has been done while the author was a National Research Fellow in Physics.

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* E. Einsporn, 'Zs. f. Phys.,' vol. 5, p. 218 (1921).